Improvements in the Early Strength Properties of Portland Cement [and Discussion]

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Improvements in the early strength properties of Portland cement

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The fuel savings that can be achieved in the manufacture of Portland cement clinker by means of mineralizers are relatively small. Further, the most effective mineralizers such as fluorine are known to have adverse effect on cement quality. However, research has shown that the retention of controlled levels of mineralizers in Portland cement clinker can result in significant quality improvements and this may provide a greater incentive for their use. The mode of action of one particular mineralizer combination is discussed and results are illustrated with reference to clinkers prepared both in the laboratory and on the production scale.

1. Introduction

In cement making, the term mineralizer is used to describe substances that facilitate the sintering reactions that take place in the rotary kiln. These substances may be added to the raw mix or may be inherent in the raw materials at certain locations.

Two examples of mineralizers whose actions are well reported in the literature are fluorides, such as CaF_2, AlF_3 (Lea 1970; Eitel 1966) and calcium sulphate (Budnikov *et al.* 1966; Butt *et al.* 1974). The beneficial effect of fluorine upon combination is thought to arise both from a reduction in the temperature of initial melting (Heinmann *et al.* 1970) and from the formation of intermediate phases whose decomposition products readily form the clinker minerals (Gilioli *et al.* 1979; Gutt *et al.* 1970). Diffusion experiments (Johansen *et al.* 1979) have also indicated that the rate of C_3S formation may be accelerated by the increased width of the C_3S primary phase region in the $C–S–CaF_2$ system compared to that in the $C–S–A–F$ system.

Similarly, the mineralizing action of SO_3 may be attributed to an increase in the quantity of the liquid phase essential for the sintering and homogenization of the clinker and to the formation of an intermediate sulphosilicate phase (Gutt *et al.* 1967).

Recent publications (Sarkar *et al.* 1980; Klemm *et al.* 1980; Kumar *et al.* 1981) have indicated an increased level of interest in the use of mineralizers, which can be attributed to a desire to reduce clinkering temperatures and achieve fuel savings. However, although the clinkering temperature required for satisfactory combination may be reduced by as much as 200 °C, when heat recuperation from the clinker cooler is considered, the potential energy savings are relatively small (Gardeik 1981); under 5 % for a 200 °C reduction in burning-zone temperature. Incentives to use mineralizers may therefore come from other considerations such as extended refractory life, reduced power consumption for raw mix preparation or improvements in cement quality.

From the literature, prospects of achieving the latter benefit with either fluorine or SO_3 appear slight. When incorporated in Portland cement clinker, fluorine is known to have an adverse effect on cement reactivity leading to extended setting times and reduced early

strengths. It has also been reported that when SO_3 entered into solid solution with C_3S its hydraulic activity was impaired (Welch *et al.* 1960). When both SO_3 and fluorine were present the combined effect resulted in very low strengths.

However, during the development of a new type of expansive cement (Pollitt & Brown 1975) we discovered that provided fluorine (normally as CaF_2) and SO_3 (normally as $CaSO_4$) were used together and in the correct proportions (Murray & Brown 1978), cements could be produced with significantly improved strength properties.

This paper describes the development of high early strength mineralized cements. The potential for strength improvements, when controlled levels of mineralizers are retained within the clinker, is illustrated with reference to clinkers prepared both in the laboratory and on the production scale.

2. DISCOVERY OF POTENTIAL FOR IMPROVED STRENGTH PROPERTIES

The shrinkage of hydrated Portland cement paste on drying is an inherent characteristic, which combined with its low tensile strength, results in crack formation in many structures. To overcome this disadvantage, several types of expansive or shrinkage compensating cements have been developed, some of them deriving their expansive properties from the hydration of uncombined magnesia or lime. Generally, these suffer from the disadvantage that the lime or magnesia either hydrates prematurely before adequate hydrate structure has been developed, resulting in loss of expansive forces, or too late, resulting in cracking of the hardened concrete. To overcome these disadvantages a cement was developed that utilized the sulphate stabilization of C_2S first reported in the literature by workers at the Building Research Establishment (Welsh *et al.* 1968) but which had been recognized within the industry as a feature of sulphate rich material in clinker derived from kiln deposits. To produce this novel cement, sufficient calcium sulphate was added to a high silica ratio, low iron mix to stabilize C_2S to an intermediate temperature of *ca.* 1480 °C. Above this temperature, loss of stabilization coincident with desulphation resulted in the formation of C_3S with a characteristic microstructure in which free lime occurred as inclusions within the alite. This structure has the advantage that not only is the size of the free lime crystals closely controlled but also they are progressively exposed as the C_3S hydrates, and consequently the expansive forces, are generated in step with strength growth. Unlike alternative expansive cement systems in which the expansive reaction takes place after silicate hydration, and which are consequently fundamentally unsound, the encapsulated free lime approach yields a stable matrix.

During the development work, calcium fluoride was added to the sulphated raw mixes and it was quickly discovered that fluorine overcame the stabilizing effect of SO_3, resulting in a more normal type of clinker microstructure. However, the benefits were that clinkers with very high C_3S contents (*ca.* 80 %) could be combined at temperatures considerably lower than those required for typical ordinary Portland cement raw mixes and further, the cements gave exceptionally high strengths at 7 days and beyond. By controlling closely the levels of SO_3, fluorine and alkali metal oxides retained in the clinker, cements could be prepared with both early and late strengths considerably higher than those of current cements at the same specific surface area.

3. Combined mineralizing action of sulphate and fluoride

At the Research Division of Blue Circle Industries the ease with which a raw mix combines to give a satisfactory level of residual free lime (hereinafter referred to as combinability) is determined by a standard test. Small uniformly sized pellets of raw mix ground to a controlled fineness, or range of finenesses, are fired under a dynamic heating régime to a range of final temperatures. The final temperatures required to give free lime levels of 1 % and 2 % are determined by interpolation. These are referred to as the 1 % and 2 % free lime combinability temperatures.

Table 1. Influence of mineralizer proportions on combinability of works' raw mix

mineralizer addition to raw mix		clinker free lime (%)				combinability temperature for 2% free lime/°C
gypsum (%)	CaF$_2$ (%)	1350 °C	1400 °C	1450 °C	1500 °C	
nil	nil	—	8.3	5.5	3.4	1550
2.0	0.25	6.3	4.0	2.4	—	1470
2.0	0.50	5.0	3.7	2.0	—	1450
4.0	0.25	5.4	4.1	2.1	—	1460
4.0	0.50	5.2	3.1	1.7	—	1440
6.0	nil	5.2	4.0	2.3	—	1460
6.0	0.25	3.9	3.0	1.8	—	1440
6.0	0.50	2.4	1.7	1.6	—	1370

Table 1 illustrates the influence of the mineralizers calcium fluoride and gypsum upon the combinability of a works' raw mix. The lime saturation factor (l.s.f.), silica ratio (s.r.) and alumina ratio (a.r.) of this sample were 99 %, 2.57 and 2.53 respectively, where

$$\text{l.s.f.} = \frac{\text{CaO}}{2.8\,\text{SiO}_2 + 1.2\,\text{Al}_2\text{O}_3 + 0.65\,\text{Fe}_2\text{O}_3},$$

$$\text{s.r.} = \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3},$$

$$\text{a.r.} = \frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3}.$$

Without the addition of mineralizers, combinability was difficult and required a final burning temperature of 1550 °C to reduce the level of uncombined lime to 2 %. The addition of the mineralizer pair of gypsum and calcium fluoride enabled free lime levels of 2 % to be attained at temperatures as low as 1370 °C. The lowest combinability temperature for 2 % free lime was obtained with the highest level of mineralizer addition shown in table 1. Higher levels, particularly of calcium fluoride could lower this temperature still further but clinker fluorine levels of greater than *ca.* 0.25 % are undesirable on quality grounds, as discussed in §5.

With the raw mix chosen to illustrate the effectiveness of the mineralizer pair, gypsum when used alone had a mineralizing action. However, as reported by Gutt & Smith (1968), and as exploited in the expansive cement described earlier, in certain compositions sulphate stabilization of C$_2$S can occur, leading to very difficult combinability. This effect is likely to occur with raw mixes low in iron oxide or alkali metal oxides, and particularly where there is a low content of K$_2$O relative to Na$_2$O.

In practice, gypsum additions to the raw mix are limited both by the SO_3 level of the final cement, which is restricted by national standards, and production aspects such as the formation of build-ups in the kiln or preheater.

On the basis of these and other results, an optimum mineralizer addition of 6 % gypsum and 0.5 % calcium fluoride was selected. This is appropriate to the method of clinker production employed in the laboratory. In large scale production kilns these levels would have to be modified on account of different levels of volatile retention according to process type.

TABLE 2. RESULTS ILLUSTRATING POTENTIAL FOR INCREASED C_3S CONTENTS

chemical parameters		mineralizer addition to raw mix		combinability temperature for 2 % free lime/°C	clinker free lime (1400 °C) (%)	clinker‡ C_3S (1400 °C) (%)
l.s.f. (%)	s.r.	gypsum (%)	CaF_2 (%)			
101	2.5	6.5	0.5	1360	1.3	58
102	2.9	6.5	0.5	1360	1.3	60
102	4.0	6.5	0.5	1380	1.6	65
102	5.8	6.5	0.5	1470	2.9	65
102	5.8†	6.5	0.5	1420	2.1	69
100	2.5	nil	nil	1550	8.3	38

† Raw feed residue reduced from 10 % to 5 % retained on 90 μm mesh.
‡ Calculated according to Bogue, taking both clinker free lime and SO_3 into account.

Table 2 indicates the manner in which a marked increase in clinker C_3S level can be achieved by using the mineralizer pair to achieve combination in mixes of high l.s.f. At a s.r. of 6 (the highest investigated) it was found advantageous to reduce the size of the raw mix residue from 10 % to 5 % retained on 90 μm. Even at this fineness, a non-mineralized mix with a s.r. of 6 and l.s.f. of 102 % required two firings at 1550 °C with intermediate crushing and grinding to bring the free lime level below 2 %. The results illustrate how the mineralizer pair enable high C_3S clinkers to be combined at temperatures lower than those required for most ordinary Portland cement (O.P.C.) clinkers.

4. INFLUENCE OF MINERALIZERS ON REACTION SEQUENCE DURING FIRING

To gain a better understanding of the reaction sequence and intermediate phases formed during the firing of mineralized compositions, a raw mix was fired to a range of intermediate temperatures at a heating rate of 10 °C/min and the phases present identified by X-ray diffraction. The chemical analysis of the raw mix studied is given in table 3. Potassium oxide was added as K_2SO_4 to control the K_2O/SO_3 ratio; the relevance of this to cement properties is discussed later.

The phases detected by powder X-ray diffraction and the temperature ranges over which they occurred are illustrated in figure 1. Note that the phases found coexisting are unlikely to represent equilibrium phase assemblages as the samples were not held at the final burning temperature. It should also be remembered that some of the phases will not have been present at the temperatures indicated, but formed during subsequent cooling.

C_3S was first detected after firing to 1250 °C. The appearance of this phase coincided, as

expected, with a decrease in the quantity of C_2S but also in the disappearance of the fluoro-aluminate phase $C_{11}A_7 \cdot CaF_2$ and the appearance of C_3A. The disappearance of $C_{11}A_7 \cdot CaF_2$ may be due to removal of fluorine from the interstitial phase by C_3S, as suggested by Klemm et al. (1980).

Klein's compound $C_4A_3\bar{S}$ had a relatively wide temperature range of occurrence as an intermediate phase but was not detected in samples fired above 1350 °C. This is consistent with its absence from mineralized clinkers prepared both in the laboratory and on the production scale.
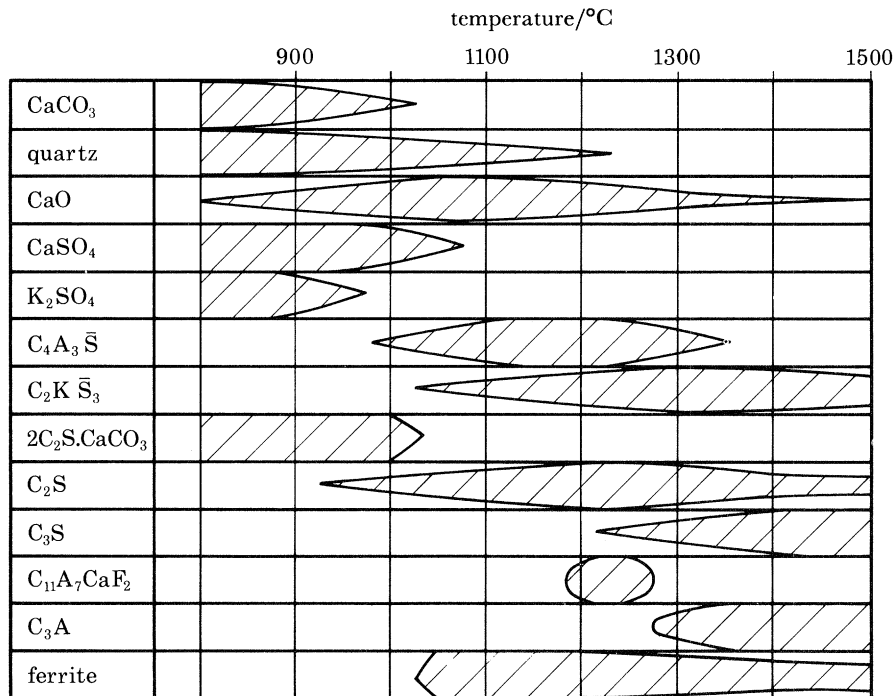

FIGURE 1. Temperature range of occurrence of phases in mineralized high C_3S composition. Samples were heated from 800 °C at a rate of 10 °C/min. Key: $C_4A_3\bar{S}$, Klein's compound; $C_2K\bar{S}_3$, calcium langbeinite; $2C_2S \cdot CaCO_3$, spurrite.

TABLE 3. RAW MIX COMPOSITION

	%		%
SiO_2	14.6	K_2O	0.78
Al_2O_3	1.8	Na_2O	0.02
Fe_2O_3	0.62	F_2	0.16
Mn_2O_3	0.04		
P_2O_5	0.04	l.s.f. (ignoring SO_3)	102
TiO_2	less than 0.01	s.r.	6.03
CaO	44.3	a.r.	2.90
MgO	0.27		
LOI	34.8	clinker potential C_3S	86.5
SO_3	2.3	(ignoring SO_3)	

Raw mix residue 1 % with 90 μm mesh.

At temperatures above 1350 °C the phases present were C_3S, C_2S, C_3A, ferrite (C_4AF) and the double salt $C_2K\bar{S}_3$ known as calcium langbeinite. This salt plays an important role in controlling the early hydration reactions as it provides a source of soluble calcium sulphate.

The C_3S phase was invariably present as the rhombohedral form in these mineralized clinkers. This has been confirmed both by X-ray diffraction and by differential thermal analysis, which shows no inversion over the temperature range 20–1000 °C. In a study reported elsewhere (Aldous 1983) the levels of fluorine and Al_2O_3 necessary to stabilize this form have been investigated. An association between rhombohedral alite and enhanced strengths has already been detected from a study of production clinkers (Goudin *et al.* 1980). Our own investigations, using conduction calorimetry, indicate that the rhombohedral form as stabilized by Al_2O_3 and fluorine is significantly more reactive than either the monoclinic or triclinic forms.

5. Properties of laboratory prepared cements

To investigate fully the strength properties of these cements, sufficient quantities of clinkers were prepared in the laboratory for full scale testing according to BS 4550. The parameters investigated included l.s.f., s.r., a.r., and the level of SO_3, fluorine and alkali metal oxides retained in the clinker. The scope of this paper does not permit a discussion of all of the results obtained. Instead this will be restricted to the influence of the variables, a.r. and fluorine content.

The cements prepared in the investigation were all ground to a surface area of 450 m^2 kg^{-1} and used to make concrete specimens at a water/cement ratio (w/c ratio) of 0.55. This is lower than the normal 0.60 w/c ratio employed in standard tests, but was necessary because of the excellent workability characteristics of the mineralized cements, which arise in part from the integral set control provided by the calcium langbeinite present in the clinker.

The presence of sufficient calcium langbeinite in the clinkers for adequate set control has two advantages. First, no gypsum need be added at the grinding stage thus eliminating problems arising from variable degrees of gypsum dehydration. Second, the release of K^+ and SO_4^{2-} ions has a pronounced accelerating effect on early hydration. Normally, the accelerating action of alkali sulphate is accompanied by a marked reduction in strength at later ages. However, in these fluorinated clinkers the strength penalty accompanying an increase in clinker alkali content is relatively small and late strengths equal to or higher than those of current cements are easily attained. For comparison purposes, typical quality results for a U.K. rapid hardening cement (R.H.P.C.) ground to a surface area of 450 m^2 kg^{-1} are given in table 4.

TABLE 4. TYPICAL STRENGTH LEVELS GIVEN BY U.K. RAPID HARDENING CEMENT (R.H.P.C.)

age/day	1	3	7	28
compressive strength/(N mm^{-2})	15	28	35	47

(Slump 35 mm.) Cement tested according to BS 4550 at a w/c ratio of 0.60.

One disadvantage associated with integral set control provided by calcium langbeinite is a tendency for coating to form on the mill lining and grinding media during cement grinding, leading to a reduction in grinding efficiency. This can be overcome by high efficiency closed circuit grinding.

Influence of a.r. ratio on strength properties

Results indicating the influence of a.r. at a s.r. of 4 are shown in table 5. The a.r. was found to have a marked influence on strength development at 8 h and 16 h but to have little effect beyond 1 day. Increases in early strength with increasing a.r. (i.e. increasing C_3A content) have

TABLE 5. INFLUENCE OF CLINKER a.r. RATIO ON QUALITY OF MINERALIZED CEMENTS

clinker chemical parameters				
K_2O (%)	1.5	1.4	1.4	1.5
SO_3 (%)	3.9	3.4	3.3	4.0
F_2 (%)	0.17	0.18	0.17	1.17
a.r.	0.46	0.93	1.9	3.6
free lime (%)	1.6	1.4	1.8	2.6
setting properties				
standard consistency water (%)	30.5	30.5	31.0	31.5
initial set/min	170	165	120	90
final set/min	215	220	145	115
concrete strength†/($N mm^{-2}$)				
8 h	1.8	4.2	8.7	11.5
16 h	18.7	23.1	25.9	28.5
24 h	31.0	34.3	34.9	34.1
3 d	47.5	47.2	48.5	46.6
7 d	56.6	54.0	54.8	53.2
28 d	61.9	63.3	62.2	60.1
slump/mm	20	21	16	16

Raw mix residue < 2% with 90 μm mesh; l.s.f. 100%; s.r. 4; cement surface area 450 m² kg⁻¹.
† Water/cement ratio 0.55.

TABLE 6. INFLUENCE OF CLINKER FLUORINE CONTENT ON THE QUALITY OF MINERALIZED HIGH SILICA RATIO CEMENTS

clinker chemical parameters							
K_2O (%)	1.0	1.2	1.4	1.5	1.4	1.2	1.5
SO_3 (%)	2.9	3.4	3.3	3.6	3.2	2.8	3.9
F_2 (%)	0.06	0.10	0.14	0.22	0.39	0.80	1.7
free lime (%)	3.3	2.0	1.7	1.7	1.6	1.5	1.1
setting properties							
standard consistency water (%)	25.3	31.0	29.0	29.5	27.5	27.5	29.5
initial set/min	90	140	155	170	240	210	540
final set/min	110	175	205	220	310	260	660
concrete strength†/($N mm^{-2}$)							
8 h	6.7	5.4	3.7	4.6	1.7	1.8	—
16 h	17.7	20.8	19.7	22.2	15.6	14.5	1.6
24 h	22.9	30.0	29.3	33.2	26.6	19.4	11.6
3 d	33.9	41.9	43.2	46.5	47.5	44.6	38.6
7 d	42.3	48.2	50.2	52.0	55.3	57.1	46.8
28 d	51.9	54.0	56.2	60.7	65.9	66.4	56.0

Raw mix residue < 2% with 90 μm mesh; l.s.f. 98%; s.r. 6; a.r. 2.5; cement surface area 450 m² kg⁻¹.
† Water/cement ratio 0.55.

been noted previously but not to the extent found in this study. At 8 h the strength given by the cement with an a.r. of 3.6 was similar to that given by current O.P.Cs at 24 h.

Influence of fluorine content on strength properties

Results of strength tests are summarized in table 6. The reduction in hydraulic activity at early ages reported by previous workers was confirmed at high levels of fluoride addition. One day strengths, however, reached a maximum at a clinker fluorine level of *ca.* 0.25% and this improvement was greater than could be accounted for by the increased level of combination (as evidenced by clinker-free lime) arising from the mineralizing action of fluorine.

It is interesting to note that at later ages this optimum clinker flourine level become progressively higher. This may be analogous to the phenomenon of increased late strength commonly found when the rate of hydration at early ages is reduced by low temperature curing conditions or the use of retarders. Further evidence for the reduction in early hydraulic activity accompanying the increase in clinker fluorine levels comes from the progressive increase in setting times.

TABLE 7. QUALITY OF CEMENTS PREPARED FROM CLINKER PRODUCED IN A SUSPENSION PREHEATER KILN

trial number		1	2
clinker chemical parameters			
l.s.f. (%)		97.7	101.6
s.r.		3.7	3.4
a.f.		2.5	2.7
K_2O (%)		1.4	1.3
SO_3 (%)		4.0	3.3
F_2 (%)		0.19	0.25
free lime (%)		1.2	1.5
cement surface area/($m^2\ kg^{-1}$)	488	322	450
setting properties			
standard consistency water (%)	29.5	26.0	—
initial set/min	160	160	—
final set/min	180	175	—
		concrete strength†/(N mm^{-2})	
8 h	3.2	—	—
16 h	19.1	—	—
24 h	29.4	21.7	25.7
3 d	40.6	33.7	39.0
7 d	46.2	39.3	45.1
28 d	53.3	46.4	51.0
slump/mm	55	50	55

† Water/cement ratio 0.60.

Even at the highest clinker fluorine level the phase $C_{11}A_7 \cdot CaF_2$ was not detected in the clinker. This phase was only found at burning temperatures below 1350 °C or when slow cooling was employed from higher temperatures.

6. PROPERTIES OF CEMENTS PREPARED FROM PRODUCTION CLINKERS

The potential strength improvements indicated by the laboratory work have been confirmed on the production scale with both wet process and suspension preheater plants. Concrete strength results obtained with clinkers sampled from two production trials on a suspension preheater plant are summarized in table 7. The strength results obtained with laboratory prepared clinkers were confirmed or even exceeded in some cases.

Figure 2 compares the strength development of cement prepared from mineralized clinker with that of current typical R.H.P.C.; both cements have a surface area of 450 m² kg⁻¹. Under standard laboratory test conditions at a fixed w/c ratio, compressive strengths up to twice those of current R.H.P.Cs can be achieved. When concretes are gauged to constant slump the superior workability characteristics of the mineralized cements give even greater benefit to strength.

7. Summary and conclusions

The mineralizer pair of fluorine and SO_3 can be employed to produce cements with early strength properties markedly superior to those of current Portland cements. This is attributable partly to the higher alite content permitted by the mineralizing action but also to increased hydraulic activity associated with the occurrence of alite as the rhombodedral polymorph, and the presence of controlled levels of readily soluble alkali sulphate.
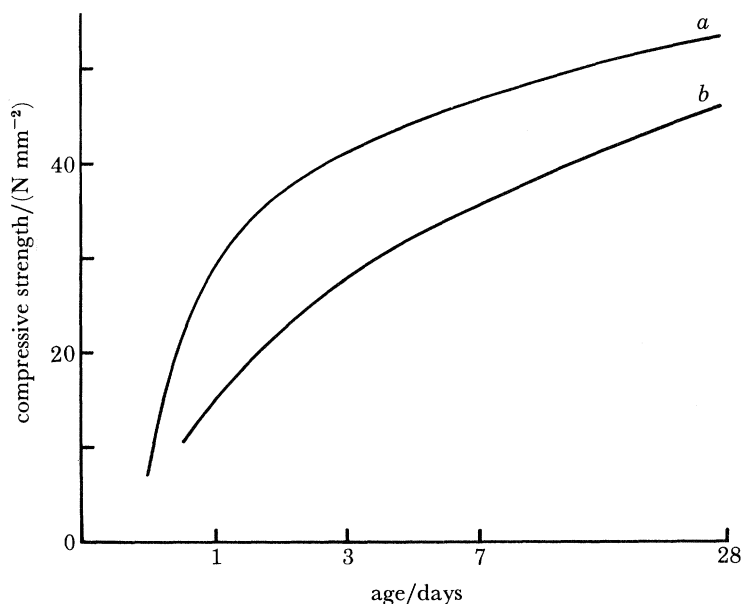

FIGURE 2. Strength development of mineralized cements prepared from production trial clinker. Tests made on 100 mm concrete cubes cured at 20 °C with mix 1:2.5:3.5:0.60. (a) Mineralized cement; (b) typical U.K. R.H.P.C.; both cements had surface area 450 m² kg⁻¹.

It is not suggested that cements of this type be employed as a replacement for current Portland cements in conventional concrete structures. Principal applications are expected to lie in two main areas. First, in the manufacture of cement based products where the high early strength development should enable considerable economies to be made, both in curing and in the turn of forming moulds. Second, in the manufacture of extended cements where the clinker is partially replaced by materials such as pulverised fuel ash or granulated blast-furnace slag. The high level of hydraulic activity of these mineralized clinkers overcomes one of the principal disadvantages of this type of cement, namely low early strength, and permits increased levels of clinker replacement and consequently increased energy savings.

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Discussion

H. F. W. TAYLOR (*University of Aberdeen, U.K.*). What is the physical state of the calcium langbeinite in the ground cement? Is it present as separate particles, or in the same particles as silicate and aluminate phases and perhaps surrounded by them? This would presumably affect its behaviour as a setting control agent.

G. K. MOIR. In the mineralized clinker the calcium langbeinite occurs in the interstitial phase. Examination of cement with a scanning electron microscope indicates that the calcium langbeinite is widely distributed as a thin layer on the surface of the cement particles. It is certainly readily accessible to water and typically *ca.* 90 % of the total K_2O content of this type of cement is extracted in water by using the method described by Pollitt *et al.* (1968).

F. MASSAZZA (*Italcementi S.p.A., Bergamo, Italy*). Sometimes we use mineralizers such as $CaSO_4$ and CaF_2 to improve burnability or other properties of clinker, but not to improve early strengths of cement. Do you believe that the cost of addition can be justified solely by the improvement in early strength?

G. K. MOIR. The improvements in early strength reported will only be achieved if closely controlled levels of SO_3, fluorine and alkalis are retained in the clinker. If improvements in early strength have not been experienced then this may be because the levels retained in your clinkers are somewhat removed from the optimum.

Whether the cost of additives can be justified solely on cement quality considerations depends on market conditions and in particular whether a premium product can be sold at a premium price. But certainly in some circumstances the additional raw material cost will be justified.

J. E. BAILEY (*University of Surrey, U.K.*). Are strength increases primarily due to increases in alite reactivity or do the aluminate phases play an increased role?

G. K. MOIR. We consider that alite reactivity is a prime factor leading to increased strength, although for early strength, the alkali and sulphate content of the clinker is very important.

Cements with a high ratio of C_3A to ferrite phase show improved early strength as is indicated in table 5 of this paper. However, it is not known whether this arises from a direct contribution to strength made by aluminate hydrates or from the influence of the increased quality of aluminate phase upon alite hydration. The presence of fluorine in these clinkers also appears to promote solid solution of alumina in C_3A and this may have a role in improving strength properties.

S. CHANDA (*University of Surrey, U.K.*). I would like to know if you have determined any other mechanical properties of these mineralized cements, such as modulus of rupture or the Young modulus, which may be of use from an engineering point of view?

G. K. MOIR. These have not been determined to date. However, the products of hydration of the mineralized cements are essentially the same as those formed by ordinary Portland cement although produced more rapidly and in slightly different proportions, and we would not expect any significant difference in mechanical properties.

P. PICHAT (*CDF Chimie, Paris, France*). First, what percentage of gypsum is added to the mineralized clinker? Second, can Dr Moir say at what industrial stage he is at, at the research or at the pilot stage? Third, has Dr Moir any experience with phosphogypsum, which contains about 0.6% fluorine?

G. K. MOIR. First, no gypsum is usually added to the mineralized clinker. The best results are obtained with the integral set control provided by calcium langbeinite when no gypsum is added at the cement grinding stage.

Second, successful trials have been done on full scale production plants.

Third, when used as a retarder, phosphogypsum can give problems associated with prolonged setting times unless the level of soluble phosphate in the gypsum is maintained below certain levels. However, when added to the raw mix the phosphate is combined within the clinker and at the levels likely to be encountered has no discernible effect on cement properties. Any fluorine contributed by the gypsum when added to the raw mix is an additional bonus. Thus, mineralization according to the method outlined in our Patent (U.K. no. 1498057, 1978) permits the use of by-product gypsums, which are not suitable for use as conventional cement retarders.

DELLA M. ROY (*Materials Research Laboratory, The Pennsylvania State University, Pennsylvania, U.S.A.*). Concerning the hydration products from those cements having relatively high sulphate contents, are the long-term hydration products enriched in ettringite content relative to normal cements? This could affect their longer term performance.

G. K. MOIR. As might be expected, whether ettringite persists depends on the ratio of SO_3 to the aluminate phases. In cements with a high s.r. (*ca.* 6) and SO_3 level of 3.5% we have found ettringite persisting at 90 days with no evidence of conversion to monosulphate. Concrete specimens have now been stored for up to 7 years with no evidence of unsoundness.

S. SPRUNG (*Research Institute of the German Cement Industry, Düsseldorf, F.R.G.*). (1) Does the addition of gypsum cause an increase in SO_2 emission?

(2) Does the addition of a fairly high amount of CaF_2 to the raw mix cause emission of HF?

(3) The addition of fluxes increase the proportion of melt in the clinker. Did Dr Moir observe or measure an increase of power consumption (kWh/t cement) during milling of the cement?

(4) Lowering the temperature in the sintering zone leads to a decrease in thermal efficiency of the clinker cooler. Did Dr Moir measure the heat consumption (kJ/kg) of the kiln system (kiln and preheater and cooler) with and without addition of fluxes?

G. K. MOIR. (1) Not necessarily. SO_2 emission will depend upon process type and upon the lowering of burning zone temperatures and consequently of SO_3 volatilization, which the mineralizers permit.

(2) I would have to refer Dr Sprung here to his own paper (Sprung *et al.* 1968) in which he concludes that the exit gases of cement kilns cannot contain gaseous fluorides. We find very little volatilization of fluoride within the kiln system and any fluorine leaving the system does so as CaF_2 in which form it is insoluble and harmless.

(3) The mineralized clinkers described are generally softer and more porous than conventional clinkers. This is because of their generally lower conventional flux content as a result of the higher s.r's permitted, and also because of the lower burning temperatures.

However, when no gypsum is added during cement grinding a marked increase in specific power consumption can occur unless the mill is equipped with an efficient closed circuit milling system. This drop in grinding efficiency arises as a result of coating formed on the mill and media.

(4) During a continuous period of production of 8 days on a 35 t/h suspension preheater plant an overall net fuel saving of about 8 % was achieved. Kiln temperature throughout was also slightly higher. No separate measure of cooler efficiency was made.

Reference

Pollitt, H. W. W. & Brown, A. W. 1968 In *5th International Symposium on the Chemistry of Cement, Tokyo,* pp. 322–333.